

# An electrochemical ionic liquid membrane reactor for NO<sub>x</sub> selective separation under excess oxygen conditions

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**Abstract** A novel electrochemical ionic liquid membrane reactor capable of separating NO from a mixture of NO and oxygen with high current efficiency at low temperatures was designed and tested. This reactor consists of a combination of an ionic liquid and a thin film of anodised alumina with two platinum electrodes. During operation of the reactor, NO is electrically transported from the cathode side to the anode side.

**Keywords** Electrochemical membrane reactor · Ionic liquid · Nitric monoxide · Anodised alumina

## 1 Introduction

There is currently a requirement for novel technologies which allow the removal of NO<sub>x</sub> under excess oxygen conditions. For this reason, numerous studies into NO<sub>x</sub> removal have been performed and more are currently in progress. Examples include the intensive study of both NO<sub>x</sub> direct decomposition catalysts and NO<sub>x</sub> selective catalysis employing urea and hydrocarbons [1–3]. To date, however, a single effective method has not been identified, primarily due to the difficulty of efficiently reducing NO in the presence of high concentrations of oxygen.

More recently, technologies involving the electrochemical reduction of NO have been studied [4, 5]. These processes use electrochemical cells to remove residual oxygen atoms from active sites using oxygen ion conductor, thus

allowing the reduction of NO to N<sub>2</sub>. These cells typically function at temperatures in excess of 573 K since they incorporate solid electrolytes. Another type of electrochemical reduction of NO using protonic conductor was studied to reduce NO between 323 and 573 K in the presence of excess O<sub>2</sub> [6]. These devices require significant levels of electric power to compensate for their poor selectivity towards NO in the presence of O<sub>2</sub>. Before devices incorporating this technology can be used in practical applications, their working temperatures and power requirements must both be decreased [7, 8].

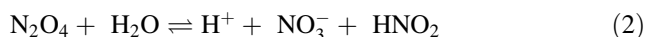
Nagao et al. [9] have studied an NO<sub>x</sub> sensor based on working and counter electrodes contained in two separate chambers. Both NO and NO<sub>2</sub> were reduced at the working electrode based on hydrogen transport through a proton conductor, and this cathodic reaction resulted in a mixed potential towards the positive potential. The working electrode meanwhile detected NO<sub>x</sub> concentrations based on the potential against the counter electrodes.

An alternate approach employing an ionic liquid/porous thin film combination has attracted considerable attention as a potential means of efficiently separating gases at low temperatures [10]. Larikov successfully separated CO<sub>2</sub> from a mixture of CO<sub>2</sub> and CH<sub>4</sub> with a selectivity ratio of 5–30 using a membrane film soaked in amine-based ionic liquids [11]. However, studies regarding the separation of NO<sub>x</sub> using this approach have not been reported.

The interaction between a liquid and NO<sub>x</sub> will typically be affected by the chemical properties of the liquid. Reaction (1), below, readily proceeds in essentially any liquid medium, while both reactions (1) and (2) occur in protic solvents. In the case of molten salts, reaction (3) occurs instead of (2).

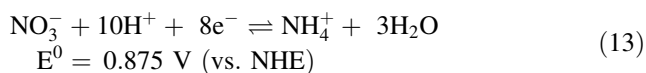
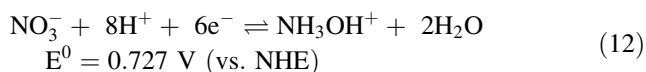
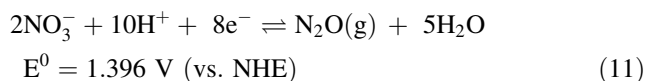
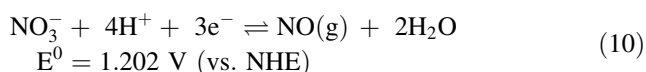
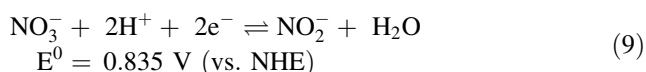
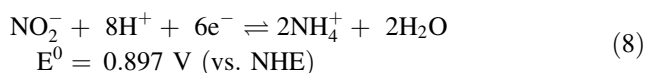
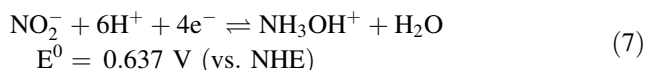
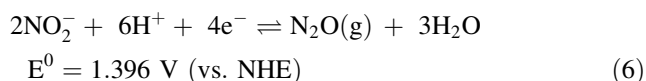
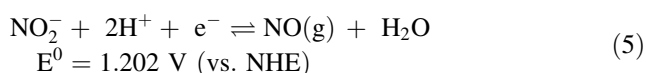
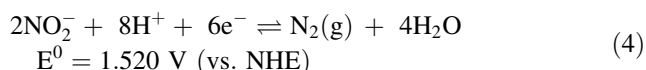


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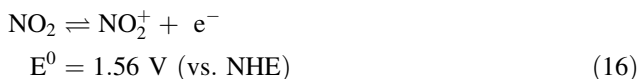
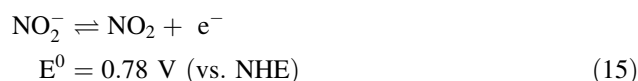
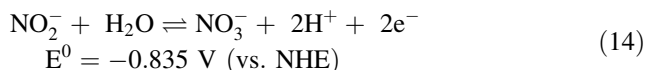


Compton et al. investigated the state of nitrite and nitrate ions in an ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or [C<sub>2</sub>mim][NTf<sub>2</sub>]) using an electrochemical technique, [10] and reported that the ions existed in a state similar to their state in molten salts. Another electrochemical study determined the solubility of nitrites and nitrates and identified some peaks related to oxidation states following contact between [C<sub>2</sub>mim][NTf<sub>2</sub>] and NO<sub>2</sub> gas [12]. These reports suggest that NO<sub>x</sub> interacts with ionic liquids primarily through reaction processes (1) and (3).

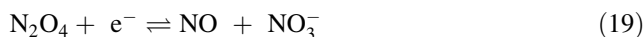
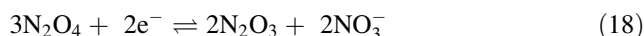
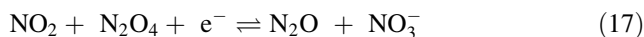
When NO<sub>x</sub> gas reacts with an ionic liquid, it dissolves in the liquid as either nitrous acid or nitric acid. The electrochemical redox reactions of nitrous and nitric acid have been reviewed in detail by Rosca et al. [13, 14], who reported the following reduction reactions of nitrous and nitric acid.



In addition, these compounds may also undergo oxidation reactions (14) and (15) in ionic liquids, as reported by Compton [12].



Reduction reactions (4) to (13) primarily occur in protic acid solvents and have not been observed in aprotic solvents. Similarly, it is expected that these reduction reactions will not occur in ionic liquids either. Boughriet et al., however, have proposed reduction reactions (17) to (20) [14].

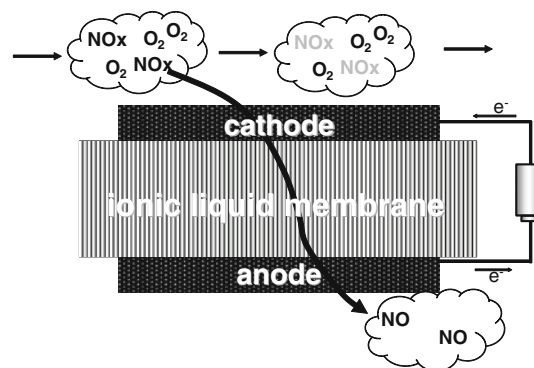


On the basis of reactions (1) to (20), we considered that it may be possible for an electrochemical membrane reactor to selectively separate NO using an ionic liquid, even under excess oxygen conditions, as in Fig. 1. If NO can be separated from an atmosphere containing oxygen at low temperatures, NO<sub>x</sub> reduction can be readily achieved because many available techniques effectively reduce NO<sub>x</sub> under oxygen-free conditions. In this study, therefore, we attempted to separate NO<sub>x</sub> under excess oxygen conditions and at low temperatures.

## 2 Experimental

### 2.1 Sample preparation

The method used for sample preparation is summarized in Fig. 2. A thin film of anodised alumina (Anodisc, 25 mm φ, 60 μm thickness, pore size 0.2 μm, Whatman, Inc.) was used

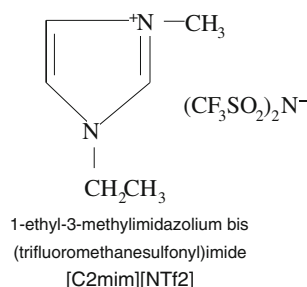


**Fig. 1** Electrochemical ionic liquid membrane reactor for selective separation of NO<sub>x</sub> under excess oxygen conditions

as the porous medium holding the ionic liquid. To improve the electronic conductivity of the electrode as well as to clean its surface, the plastic guide around the disc was removed via calcining in air at 873 K. The calcined alumina was then placed in a vacuum chamber and a 100 nm thick platinum film was sputtered on only one side. The disc was subsequently removed from the chamber and a few drops of ionic liquid were placed on the bare side. After absorption, any excess ionic liquid was removed by blowing air over the disc surface. The compound 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C<sub>2</sub>mim][NTf<sub>2</sub>], Tokyo Chemical Industry) was used as the ionic liquid (Fig. 3), since the electrochemical solubility of NO<sub>x</sub> in this liquid has already been reported [12]. Following impregnation by the ionic liquid, a 100-nm platinum film was sputtered onto the bare side. The platinum was deposited only at the surface of the anodised alumina, as shown in the reflected electron image in Fig. 2.

## 2.2 Experimental methods

In this study, NO<sub>x</sub> separation was investigated using the apparatus shown in Fig. 4. The previously prepared sample disc was held between two stainless steel electrodes using ceramic insulators and O-rings. The electrodes on either side were connected to a direct-current power source (Keithley 2400). Two different gaseous mixtures gases were circulated separately along the upper and lower sides of the apparatus and each gas could be analysed separately using a quadrupole mass spectrometer upon changing the gas flow to the instrument. A mixture of NO and O<sub>2</sub> diluted with He was circulated along the upper side, while pure He gas was circulated along the lower side to allow us to follow the permeation of NO and O<sub>2</sub> from the upper



**Fig. 3** Molecular structure of ionic liquid

chamber. The entire apparatus was placed under He to prevent air from entering into the cell. As shown in Fig. 1, during the separation of NO, NO<sub>2</sub> or N<sub>2</sub> could be detected in the He flow along the lower side.

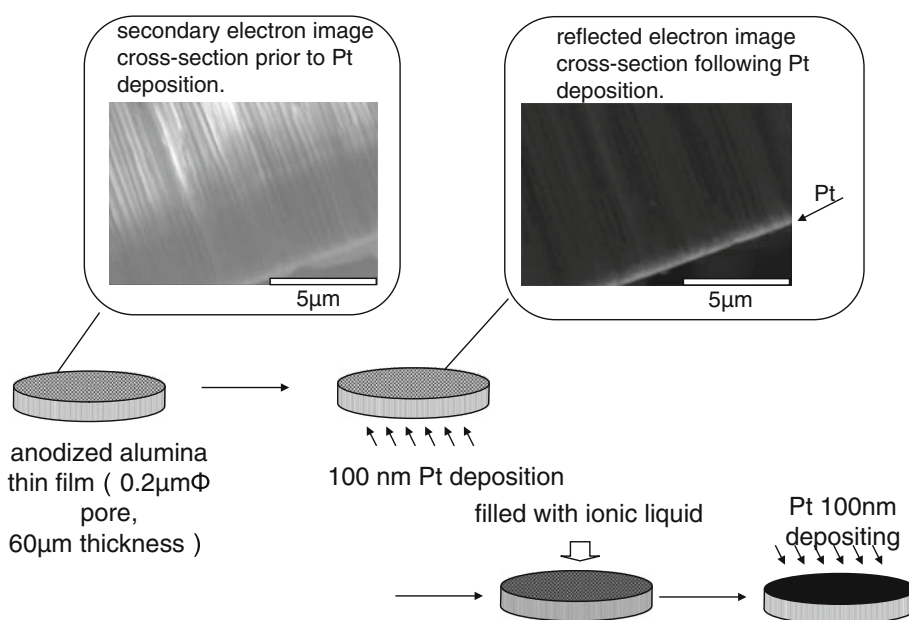
## 3 Experimental results

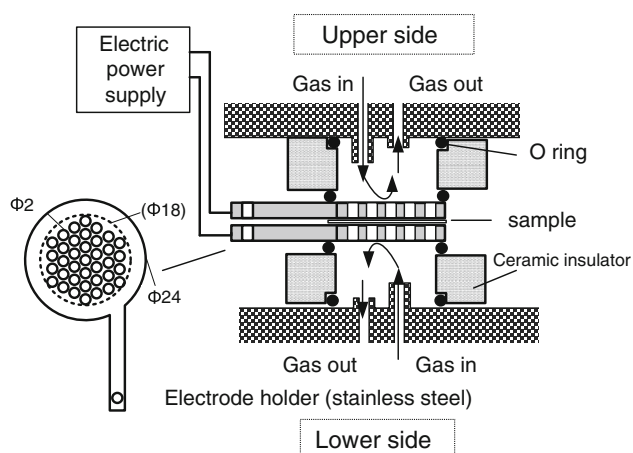
### 3.1 Cyclic voltammograms

Cyclic voltammograms (CV) were obtained at a sweep rate of 50 mV/min at 293 K, as shown in Fig. 5a, while varying the gas composition along the upper side of the apparatus. The CV profiles are essentially the same for pure He, 0.1 % NO and 10 % O<sub>2</sub>, although a noticeably different profile is obtained when a 0.1 % NO + 10 % O<sub>2</sub> mixture is circulated. When a negative voltage was applied to the upper side, this difference was enhanced.

The temperature dependencies of the CV profiles were subsequently investigated, using the 0.1 % NO + 10 % O<sub>2</sub> gas mixture, and Fig. 4 demonstrates that increasing the temperature also increases the current resulting from the

**Fig. 2** Preparation of electrochemical ionic liquid membrane





**Fig. 4** Apparatus for NO selective separation

cell. Increases in temperature will increase the diffusion of nitrate ions in  $[C_2mim][Ntf_2]$  as well as the reaction rate of NO and  $O_2$ , while decreasing the degree of NO adsorption. In this case, the increased current is primarily due to increases in nitrate ion diffusion.

### 3.2 Electrochemical NO gas separation

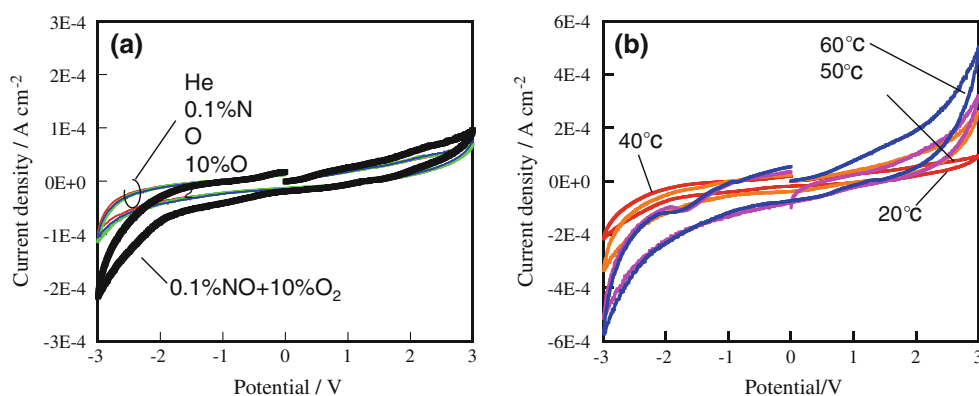
Prior to assessing the effects of the applied voltage on  $NO_x$  permeation, it is important to ensure the absence of any gas leaks in the apparatus, which helps to assess the ability of the sample disc to act as a gas barrier between the upper and lower portions of the apparatus. As an initial step, changes in NO and  $O_2$  concentrations in the lower side gas flow were monitored while 200 ppm NO + 10 %  $O_2$  flowed over the upper side without the application of any potential. Under these conditions, NO gas was not detected (Fig. 6a), but a signal corresponding to 10 ppm  $O_2$  gas was observed (Fig. 6b). The ratio at which  $O_2$  had leaked through to the lower side was calculated as 1/10,000 and we believe that this apparent leakage was caused either by desorption of dissolved gas in the ionic liquid or an insufficient gas seal. We suspect that the former was the main cause.

Based on an analysis by Broder et al. [12], the diffusion coefficient of nitrate ions in the ionic liquid is estimated to be  $10^{-10} \text{ m}^2/\text{s}$  (at 293 K). Using the cell thickness of 60  $\mu\text{m}$  and the above diffusion coefficient, on the basis of Fick's first law the proportion of nitrate ions which can pass from the upper to the lower side is 1/60,000. The expected NO concentration on the lower side was therefore estimated at 0.003 ppm, which is below the detection limit of our experimental equipment, and thus such exceedingly small NO leaks could not be detected. The diffusion coefficient of the oxygen-containing ionic liquid is not known, but if we assume that the diffusion coefficient of oxygen is of the same order as that of the nitrate ion, the  $O_2$  concentration on the lower side is expected to be on the same order as the measured concentration of a few tens of ppm.

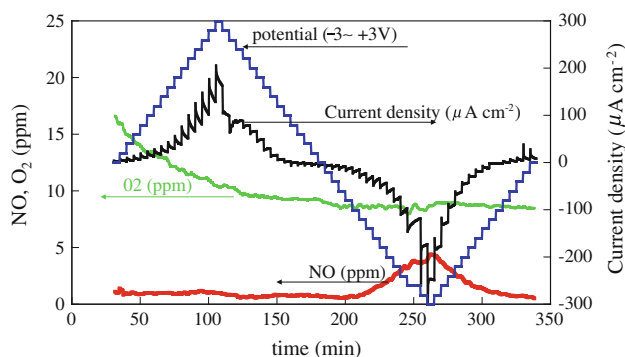
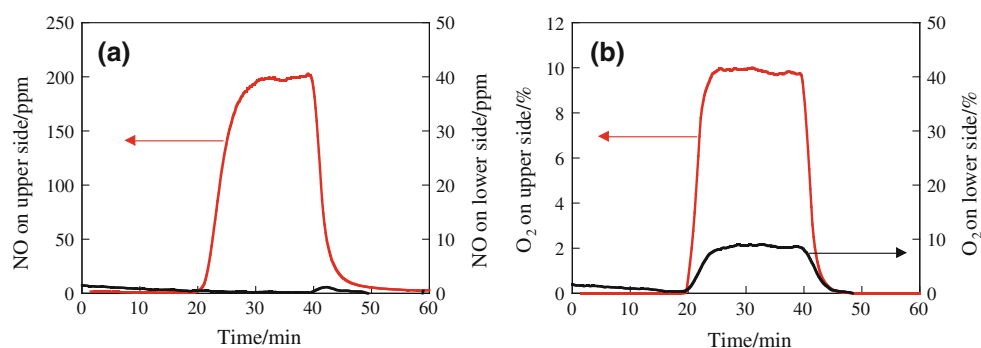
We confirmed that the leak of NO from the upper side was extremely small and so proceeded to measure the changes in gas concentration on varying the applied voltage while 200 ppm NO + 10 %  $O_2$  flowed along the upper side. The applied voltage was varied at the rate of 0.2 V/5 min (Fig. 7). The results obtained were similar to those seen in the CVs shown in Fig. 5; the CVs indicate that the current produced with a positive voltage is greater than that with a negative voltage. The concentration of oxygen decreased and eventually reached a plateau when the air in the apparatus was replaced with the gas flow. The oxygen concentration also remained constant with changes in voltage, while the concentration of NO began to increase when the potential was below  $-2 \text{ V}$ .

To eliminate the effect of applying a potential on the NO permeation rate, the variation in the NO concentration was measured at both upper and lower sides. The applied potential was set to a constant  $-3 \text{ V}$  and 200 ppm NO + 10 %  $O_2$  gas was provided along the upper side (Fig. 8). As soon as the potential was applied (at the 15 min mark in Fig. 8), the NO concentration simultaneously increased on the upper side and decreased on the lower side. After 10 min, the NO concentration on the upper side had decreased from 200 to 170 ppm, while the

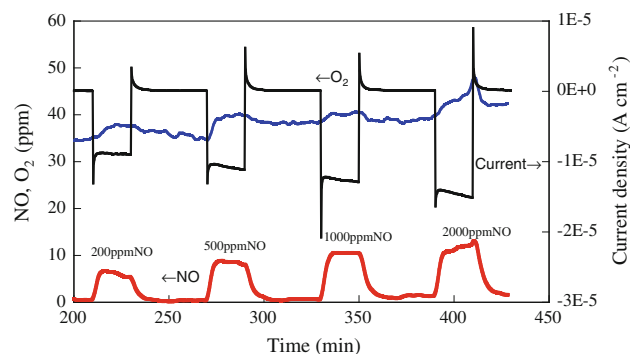
**Fig. 5** Cyclic voltammograms of the oxidation and reduction of  $[C_2mim][Ntf_2]$  showing **a** the effects of different atmospheres and **b** the effects of temperature (0.1 % NO + 10 %  $O_2$  atmosphere)



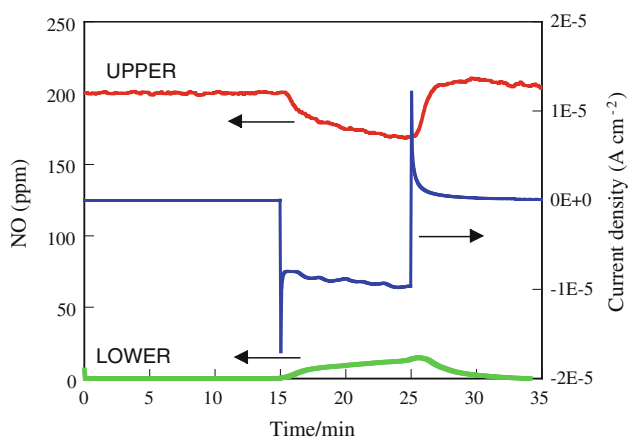
**Fig. 6** Gas leak test using 200 ppm NO + 10 % O<sub>2</sub> (323 K). **a** NO concentration and **b** O<sub>2</sub> concentration



**Fig. 7** NO and O<sub>2</sub> gas concentrations on the lower side using 200 ppm NO + 10 % O<sub>2</sub> (323 K) gas



**Fig. 9** Effect of NO concentration on NO selective separation ((200–2,000 ppm) NO + 10 % O<sub>2</sub> 323 K)



**Fig. 8** NO gas concentration and current on upper and lower side (200 ppm NO + 10 % O<sub>2</sub>, -3 V, 323 K)

NO concentration on the lower side increased to 15 ppm. The current measured during this phase was 400  $\mu$ A.

We next investigated the effects of NO concentration in the upper side gas flow. The NO concentration was increased sharply from 200 to 2,000 ppm, while the O<sub>2</sub> concentration was maintained at 10 %. The NO concentration was then measured as the degree of NO permeation (Fig. 9). Both the extent of NO and O<sub>2</sub> permeation and the current increased with an increase in the NO concentration.

### 3.3 Nitrate and nitrite ion content in ionic liquid after measurement

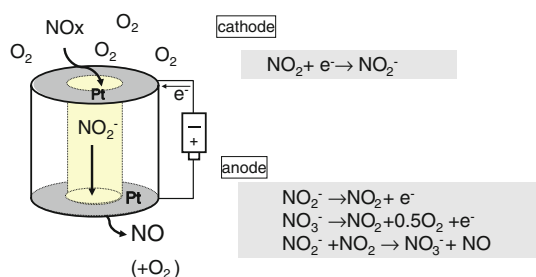
We compared the nitrate and nitrite ion content in the ionic liquid before and after NO permeation trials conducted at 3 V for more than an hour, using ion chromatography. The nitrate and nitrite ion contents were found to have increased following the experiment, and the increase in the nitrate ion content was especially significant. The degree of solubility determined for the nitrate ion was 140 mM, which is consistent with the reported values of 140 ( $\pm 10$ ) mM ([NO<sub>2</sub>]) and 46 ( $\pm 5$ ) mM [N<sub>2</sub>O<sub>4</sub>] at 298 K.

## 4 Discussion

Our experiments demonstrated the possibility of electrochemically removing NO using an anode electrode. In this section, we discuss the mechanism of NO (or NO and O<sub>2</sub>) transport, based in part on a study by Compton (Fig. 10).

When NO reacts with O<sub>2</sub> at the cathode electrode, both NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are formed. The rates of adsorption and reactivity of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> are greater than those of NO and O<sub>2</sub>, and hence NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> can dissolve in the ionic liquid in the same manner as nitrite ions by accepting electrons through reactions (21), (22) and (1).



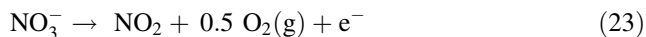


**Fig. 10** Proposed mechanism for NO selective separation



Nitrite ions dissolved in the ionic liquid are converted to  $\text{NO}_2$  after the release of an electron, as depicted on the left-hand side of reaction (1). On the basis of the experimental results, which did not detect  $\text{NO}_2$ , we contend that  $\text{NO}_2$  reacts with nitrite ions and forms nitrate ions and NO. We believe that reaction (3) can take place in the liquid phase without passing through the gaseous phase because this reaction has been observed in a nitric-based molten salt ( $\text{KNO}_3\text{--NaNO}_3$ ). As a result of reaction (3), NO was detected on the cathode side.

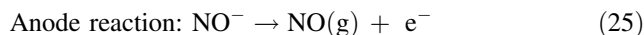
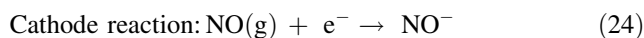
During initial experimentation using a fresh sample, only changes in NO concentration were observed following the application of a potential. However, on repeated trials, we sometimes saw variations in oxygen concentration on the cathode side after applying a potential. This occurred because the increase in nitrite ions resulted in oxygen production through reaction (23) [15]. The  $\text{NO}_2$  formed in this manner subsequently reacts again to form nitrite ions and NO via reactions (1) and (3).



The ions detected during this process were nitrite rather than nitrate, as shown in Table 1, since the nitrate ions were oxidised to nitrite upon exposure to atmospheric oxygen.

We believe that the reactor functions according to the principles described above. We also propose that the simple reaction mechanisms (24) and (25) are involved, although no study confirming these mechanisms have been identified to date. These mechanisms will be clarified as we

continue to study the interactions between ionic liquids and gases.



Finally, the efficiency of the throughput and current was estimated so as to evaluate the performance of the reactor. We estimated the amount of NO permeation per unit time and area, as well as the correlation between NO permeation per unit time and current.

Based on the data in Fig. 8, 15 ppm NO (at a total flow rate of 60 cc/min) permeated the device at a current of 400  $\mu\text{A}$ , corresponding to an estimated NO flow rate of  $0.75 \times 10^{-9}$  mol/s, while the current of 400  $\mu\text{A}$  gave an estimate of  $4 \times 10^{-9}$  mol/s. If we assume that the transport reaction involves one electron per NO molecule (as shown in Fig. 1), the current efficiency of the device is therefore  $\sim 20\%$ . We know that a high current-efficiency reactor is required to separate NO from a mixture of 1,000 ppm NO + 1 %  $\text{O}_2$  and, since the current efficiency of conventional electrochemical cells [4, 8] is around 10 %, they must operate at temperatures above 573 K. In contrast, our proposed reactor can operate with a higher current efficiency and at lower operating temperatures than conventional electrochemical reactors, although it did not demonstrate the reduction of  $\text{NO}_x$  to  $\text{N}_2$ .

## 5 Conclusion

We designed and built an electrochemical ionic liquid membrane reactor for selective  $\text{NO}_x$  separation under excess oxygen conditions and investigated its performance. The reactor consisted of an anodised alumina thin film with platinum electrodes transfused by an ionic liquid [ $\text{C}_2\text{mim}$ ][NTf<sub>2</sub>]. Permeation of NO from the cathode to the anode was observed upon applying a voltage above 2 V and only a very small amount of oxygen permeated the device along with the NO. We were thus able to demonstrate that this reactor is capable of selective  $\text{NO}_x$  separation in oxygen-rich conditions, even at low temperatures.

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**Table 1** Nitrate and nitrite ion cell contents before and after experimentation (0.021 g ionic liquid per cell)

	$\text{NO}_3^-$ ( $\mu\text{mol}$ )	$\text{NO}_2^-$ ( $\mu\text{mol}$ )
Before experiment	0.01	0.003
After experiment	2.0	0.02

Per cell (ionic liquid 0.021 g)

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